

PERFORMANCE SPECIFICATION 12A
SPECIFICATIONS AND TEXT PROCEDURES FOR TOTAL VAPOR PHASE MERCURY
CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES

1.0 Scope and Application

1.1 Analyte

ANALYTE	CAS No.
Mercury (Hg)	7439-97-6

1.2 Applicability

1.2.1 This specification is for evaluating the acceptability of total vapor phase Hg continuous emission monitoring systems (CEMS) installed on the exit gases from fossil fuel fired boilers at the time of or soon after installation and whenever specified in the regulations. The Hg CEMS must be capable of measuring the total concentration in $\mu\text{g}/\text{m}^3$ (regardless of speciation) of vapor phase Hg, and recording that concentration on a wet or dry basis. Particle bound Hg is not included in the measurements.

This specification is not designed to evaluate an installed CEMS's performance over an extended period of time nor does it identify specific calibration techniques and auxiliary procedures to assess the CEMS's performance. The source owner or operator, however, is responsible to calibrate, maintain, and operate the CEMS properly. The Director may require, under Clean Air Act (CAA) section 114, the operator to conduct CEMS performance evaluations at other times besides the initial test to evaluate the CEMS performance. See Section 1.4(c) of this text.

1.2.2 For an affected facility that is also subject to the requirements of subpart I of 40 CFR part 75* of this chapter, the owner or operator may conduct the performance evaluation of the Hg CEMS according to §75.20(c)(1)* and section 6 of appendix A to 40 CFR part 75*, in lieu of following the procedures in this performance specification.

2.0 Summary of Performance Specification

Procedures for measuring CEMS relative accuracy, measurement error and drift are outlined. CEMS installation and measurement location specifications, and data reduction procedures are included. Conformance of the CEMS with the Performance Specification is determined.

3.0 Definitions

3.1 Continuous Emission Monitoring System (CEMS) means the total equipment required for the determination of a pollutant concentration. The system consists of the following major subsystems: sample interface, Hg analyzer, and data recorder.

3.2 Sample Interface means that portion of the CEMS used for one or more of the following: sample acquisition, sample transport, sample conditioning, and protection of the monitor from the effects of the stack effluent.

- 3.3 Hg Analyzer means that portion of the Hg CEMS that measures the total vapor phase Hg mass concentration and generates a proportional output.
- 3.4 Data Recorder means that portion of the CEMS that provides a permanent electronic record of the analyzer output. The data recorder may provide automatic data reduction and CEMS control capabilities.
- 3.5 Span Value means the upper limit of the intended Hg concentration measurement range. The span value is a value equal to two times the emission standard. Alternatively, for an affected facility that is also subject to the requirements of subpart I of 40 CFR part 75*, the Hg span value(s) may be determined according to section 2.1.7 of appendix A to 40 CFR part 75*.
- 3.6 Measurement Error (ME) means the absolute value of the difference between the concentration indicated by the Hg analyzer and the known concentration generated by a reference gas, expressed as a percentage of the span value, when the entire CEMS, including the sampling interface, is challenged. An ME test procedure is performed to document the accuracy and linearity of the Hg CEMS at several points over the measurement range.
- 3.7 Upscale Drift (UD) means the absolute value of the difference between the CEMS output response and an upscale Hg reference gas, expressed as a percentage of the span value, when the entire CEMS, including the sampling interface, is challenged after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.
- 3.8 Zero Drift (ZD) means the absolute value of the difference between the CEMS output response and a zero-level Hg reference gas, expressed as a percentage of the span value, when the entire CEMS, including the sampling interface, is challenged after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.
- 3.9 Relative Accuracy (RA) means the absolute mean difference between the pollutant concentration(s) determined by the CEMS and the value determined by the reference method (RM) plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests. Alternatively, for low concentration sources, the RA may be expressed as the absolute value of the difference between the mean CEMS and RM values.
- 4.0 Interferences [Reserved]
- 5.0 Safety
- The procedures required under this performance specification may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. The CEMS user's manual and materials recommended by the RM should be consulted for specific precautions to be taken.
- 6.0 Equipment and Supplies
- 6.1 CEMS Equipment Specifications

- 6.1.1 Data Recorder Scale. The Hg CEMS data recorder output range must include zero and a high level value. The high level value must be approximately two times the Hg concentration corresponding to the emission standard level for the stack gas under the circumstances existing as the stack gas is sampled. A lower high-level value may be used, provided that the measured values do not exceed 95 percent of the high level value. Alternatively, for an affected facility that is also subject to the requirements of subpart I of 40 CFR part 75*, the owner or operator may set the full-scale range(s) of the Hg analyzer according to section 2.1.7 of appendix A to 40 CFR part 75*.
- 6.1.2 The CEMS design should also provide for the determination of calibration drift at a zero value (zero to 20 percent of the span value) and at an upscale value (between 50 and 100 percent of the high-level value).
- 6.2 Reference Gas Delivery System. The reference gas delivery system must be designed so that the flowrate of reference gas introduced to the CEMS is the same at all three challenge levels specified in Section 7.1 and at all times exceeds the flow requirements of the CEMS.
- 6.3 Other equipment and supplies, as needed by the applicable reference method used. See Section 8.6.2.
- 7.0 Reagents and Standards
- 7.1 Reference Gases. Reference gas standards are required for both elemental (Hg^0) and oxidized Hg (Hg and mercuric chloride, HgCl_2). The use of National Institute of Standards and Technology (NIST)-certified or NIST-traceable standards and reagents is required. The following gas concentrations are required.
- 7.1.1 Zero-level. 0 to 20 percent of the span value.
- 7.1.2 Mid-level. 50 to 60 percent of the span value.
- 7.1.3 High-level. 80 to 100 percent of the span value.
- 7.2 Reference gas standards may also be required for the reference methods. See Section 8.6.2.
- 8.0 Performance Specification (PS) Test Procedure
- 8.1 Installation and Measurement Location Specifications
- 8.1.1 CEMS Installation. Install the CEMS at an accessible location downstream of all pollution control equipment. Since the Hg CEMS sample system normally extracts gas from a single point in the stack, use a location that has been shown to be free of stratification for SO_2 and NO_x through concentration measurement traverses for those gases. If the cause of failure to meet the RA test requirement is determined to be the measurement location and a satisfactory correction technique cannot be established, the Director may require the CEMS to be relocated.
- Measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are listed below.
- 8.1.2 Measurement Location. The measurement location should be (1) at least two equivalent diameters downstream of the nearest control device, point of pollutant generation or other point at which a change of pollutant concentration may occur, and (2) at least half an equivalent diameter upstream

- from the effluent exhaust. The equivalent duct diameter is calculated as per Method 1 in Appendix A of this text.
- 8.1.3 Hg CEMS Sample Extraction Point. Use a sample extraction point (1) no less than 1.0 meter from the stack or duct wall, or (2) within the centroidal velocity traverse area of the stack or duct cross section.
- 8.2 RM Measurement Location and Traverse Points. Refer to PS 2. The RM and CEMS locations need not be immediately adjacent.
- 8.3 ME Test Procedure. The Hg CEMS must be constructed to permit the introduction of known concentrations of Hg and HgCl₂ separately into the sampling system of the CEMS immediately preceding the sample extraction filtration system such that the entire CEMS can be challenged. Sequentially inject each of the three reference gases (zero, mid-level, and high level) for each Hg species. Record the CEMS response and subtract the reference value from the CEMS value, and express the absolute value of the difference as a percentage of the span value (see example data sheet in Figure 12A-1). For each reference gas, the absolute value of the difference between the CEMS response and the reference value shall not exceed 5 percent of the span value. If this specification is not met, identify and correct the problem before proceeding.
- 8.4 UD Test Procedure
- 8.4.1 UD Test Period. While the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart, determine the magnitude of the UD once each day (at 24-hour intervals, to the extent practicable) for 7 consecutive unit operating days according to the procedure given in Sections 8.4.2 through 8.4.3. The 7 consecutive unit operating days need not be 7 consecutive calendar days. Use either Hg⁰ or HgCl₂ standards for this test.
- 8.4.2 The purpose of the UD measurement is to verify the ability of the CEMS to conform to the established CEMS response used for determining emission concentrations or emission rates. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and response settings, conduct the UD test immediately before these adjustments, or conduct it in such a way that the UD can be determined.
- 8.4.3 Conduct the UD test at either the mid-level or high-level point specified in Section 7.1. Introduce the reference gas to the CEMS. Record the CEMS response and subtract the reference value from the CEMS value, and express the absolute value of the difference as a percentage of the span value (see example data sheet in Figure 12A-1). For the reference gas, the absolute value of the difference between the CEMS response and the reference value shall not exceed 5 percent of the span value. If this specification is not met, identify and correct the problem before proceeding.
- 8.5 ZD Test Procedure
- 8.5.1 ZD Test Period. While the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart, determine the magnitude of the ZD once each day (at 24-hour intervals, to the extent practicable) for 7 consecutive unit operating days according to the procedure given in Sections 8.5.2 through 8.5.3. The 7 consecutive unit operating days need not be 7 consecutive calendar days. Use either nitrogen, air, Hg⁰, or HgCl₂ standards for this test.
- 8.5.2 The purpose of the ZD measurement is to verify the ability of the CEMS to conform to the established CEMS response used for determining emission concentrations or emission rates. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and response settings, conduct the ZD test immediately before these adjustments, or conduct it in such a way that the ZD can be determined.

8.5.3 Conduct the ZD test at the zero level specified in Section 7.1. Introduce the zero gas to the CEMS. Record the CEMS response and subtract the zero value from the CEMS value and express the absolute value of the difference as a percentage of the span value (see example data sheet in Figure 12A-1). For the zero gas, the absolute value of the difference between the CEMS response and the reference value shall not exceed 5 percent of the span value. If this specification is not met, identify and correct the problem before proceeding.

8.6 RA Test Procedure

8.6.1 RA Test Period. Conduct the RA test according to the procedure given in Sections 8.6.2 through 8.6.6 while the affected facility is operating at normal full load, or as specified in an applicable subpart. The RA test may be conducted during the ZD and UD test period.

8.6.2 RM. Unless otherwise specified in an applicable subpart of the regulations, use Method 29, Method 30A, or Method 30B in Appendix A of this text, or American Society of Testing and Materials (ASTM) Method D 6784-02 (incorporated by reference, see Section 1.6 of this text) as the RM for Hg concentration. Do not include the filterable portion of the sample when making comparisons to the CEMS results. When Method 29, Method 30B, or ASTM D6784-02 is used, conduct the RM test runs with paired or duplicate sampling systems. When Method 30A is used, paired sampling systems are not required. If the RM and CEMS measure on a different moisture basis, data derived with Method 4 in Appendix A of this text shall also be obtained during the RA test.

8.6.3 Sampling Strategy for RM Tests. Conduct the RM tests in such a way that they will yield results representative of the emissions from the source and can be compared to the CEMS data. It is preferable to conduct moisture measurements (if needed) and Hg measurements simultaneously, although moisture measurements that are taken within an hour of the Hg measurements may be used to adjust the Hg concentrations to a consistent moisture basis. In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period for each paired RM run (including the exact time of day) on the CEMS chart recordings or other permanent record of output.

8.6.4 Number and length of RM Tests. Conduct a minimum of nine RM test runs. When Method 29, Method 30B, or ASTM D6784-02 is used, only test runs for which the data from the paired RM trains meet the relative deviation (RD) criteria of this PS shall be used in the RA calculations. In addition, for Method 29 and ASTM D 6784-02 use a minimum sample time of 2 hours and for Method 30A use a minimum sample time of 30 minutes.

Note: More than nine sets of RM tests may be performed. If this option is chosen, paired RM test results may be excluded so long as the total number of paired RM test results used to determine the CEMS RA is greater than or equal to nine. However, all data must be reported, including the excluded data.

8.6.5 Correlation of RM and CEMS Data. Correlate the CEMS and the RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration for each RM test period. Consider system response time, if important, and confirm that the results are on a consistent moisture basis with the RM test. Then, compare each integrated CEMS value against the corresponding RM value. When Method 29, Method 30A, Method 30B, or ASTM D6784-02 is used, compare each CEMS value against the corresponding average of the paired RM values.

8.6.6 Paired RM Outliers

8.6.6.1 When Method 29, Method 30B, or ASTM D6784–02 is used, outliers are identified through the determination of relative deviation (RD) of the paired RM tests. Data that do not meet this criteria should be flagged as a data quality problem. The primary reason for performing paired RM sampling is to ensure the quality of the RM data. The percent RD of paired data is the parameter used to quantify data quality. Determine RD for two paired data points as follows:

$$RD = 100 \times \frac{|(C_a - C_b)|}{C_a + C_b} \quad \text{Eq. 12A-1}$$

where C_a and C_b are concentration values determined from each of the two samples respectively.

8.6.6.2 A minimum performance criteria for RM Hg data is that RD for any data pair must be ≤ 10 percent as long as the mean Hg concentration is greater than $1.0 \mu\text{g}/\text{m}^3$. If the mean Hg concentration is less than or equal to $1.0 \mu\text{g}/\text{m}^3$, the RD must be ≤ 20 percent. Pairs of RM data exceeding these RD criteria should be eliminated from the data set used to develop a Hg CEMS correlation or to assess CEMS RA.

8.6.7 Calculate the mean difference between the RM and CEMS values in the units of micrograms per cubic meter ($\mu\text{g}/\text{m}^3$), the standard deviation, the confidence coefficient, and the RA according to the procedures in Section 12.0.

8.7 Reporting. At a minimum (check with the appropriate EPA Regional Office, State or local Agency for additional requirements, if any), summarize in tabular form the results of the RD tests and the RA tests or alternative RA procedure, as appropriate. Include all data sheets, calculations, charts (records of CEMS responses), reference gas concentration certifications, and any other information necessary to confirm that the performance of the CEMS meets the performance criteria.

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this PS (see Section 8.0). Refer to the RM employed for specific analytical procedures.

12.0 Calculations and Data Analysis

Summarize the results on a data sheet similar to that shown in Figure 2–2 for PS 2.

12.1 Consistent Basis. All data from the RM and CEMS must be compared in units of $\mu\text{g}/\text{m}^3$, on a consistent and identified moisture and volumetric basis (STP = $20 \text{ }^\circ\text{C}$, 760 millimeters (mm) Hg).

12.1.1 Moisture Correction (as applicable). If the RM and CEMS measure Hg on a different moisture basis, use Equation 12A–2 to make the appropriate corrections to the Hg concentrations.

$$\text{Concentration}_{(\text{dry})} = \frac{\text{Concentration}_{(\text{wet})}}{(1 - B_{\text{ws}})} \quad \text{Eq. 12A-2}$$

In Equation 12A-2, B_{ws} is the moisture content of the flue gas from Method 4, expressed as a decimal fraction (e.g., for 8.0 percent H_2O , $B_{\text{ws}} = 0.08$).

12.2 Arithmetic Mean. Calculate the arithmetic mean of the difference, d , of a data set as follows:

$$\bar{d} = \frac{1}{n} \sum_{i=1}^n d_i \quad \text{Eq. 12A-3}$$

where:

n = Number of data points; and

$\sum_{i=1}^n d_i$ = Algebraic summation of the individual differences, d_i .

12.3 Standard Deviation. Calculate the standard deviation, S_d , as follows:

$$S_d = \left[\frac{\sum_{i=1}^n d_i^2 - \frac{\left(\sum_{i=1}^n d_i\right)^2}{n}}{n-1} \right]^{\frac{1}{2}} \quad \text{Eq. 12A-4}$$

12.4 Confidence Coefficient (CC). Calculate the 2.5 percent error confidence coefficient (one-tailed), CC, as follows:

$$\text{CC} = t_{0.975} \frac{S_d}{\sqrt{n}} \quad \text{Eq. 12A-5}$$

where:

$t_{0.975}$ = t-value (see Table 12A-1)

12.5 RA. Calculate the RA of a set of data as follows:

$$\text{RA} = \frac{|\bar{d}| + |\text{CC}|}{\text{RM}} \times 100 \quad \text{Eq. 12A-6}$$

where:

$|\bar{d}|$ = Absolute value of the mean differences (from Equation 12A-3);

$|\text{CC}|$ = Absolute value of the confidence coefficient (from Equation 12A-5); and

\overline{RM} = Average RM value.

- 13.0 Method Performance
 - 13.1 ME. ME is assessed at zero-level, mid-level and high-level values as given below using standards for both Hg^0 and $HgCl_2$. The mean difference between the indicated CEMS concentration and the reference concentration value for each standard shall be no greater than 5 percent of the span value.
 - 13.2 UD. The UD shall not exceed 5 percent of the span value on any of the 7 days of the UD test.
 - 13.3 ZD. The ZD shall not exceed 5 percent of the span value on any of the 7 days of the ZD test.
 - 13.4 RA. The RA of the CEMS must be no greater than 20 percent of the mean value of the RM test data in terms of units of $\mu g/m^3$. Alternatively, if the mean RM is less than $5.0 \mu g/m^3$, the results are acceptable if the absolute value of the difference between the mean RM and CEMS values does not exceed $1.0 \mu g/m^3$.
- 14.0 Pollution Prevention [Reserved]
- 15.0 Waste Management [Reserved]
- 16.0 Alternative Procedures [Reserved]
- 17.0 Bibliography
 - 17.1 40 CFR part 60, appendix B, "Performance Specification 2—Specifications and Test Procedures for SO₂ and NO_X Continuous Emission Monitoring Systems in Stationary Sources."
 - 17.2 40 CFR part 60, appendix A, "Method 29—Determination of Metals Emissions from Stationary Sources."
 - 17.3 ASTM Method D6784–02, "Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)."
- 18.0 Tables and Figures

Table 12A-1: t-Values

n^a	$t_{0.975}$	n^a	$t_{0.975}$	n^a	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145

6	2.571	11	2.228	16	2.131
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^a The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

Figure 12A-1: ME, ZD, and UD Determination

	Date	Time	Reference gas value (mg/m ³)	CEMS measured value (mg/m ³)	Absolute difference	Drift or measurement error (% of span value)
Low Level						
Mid Level						
High Level						

*Code of Federal Regulations, Title 40, Part 75